Mineral Content of Mixed Fertilizer

By Jumpei ANDO and Seiichi MATSUNO

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Recently in Japan nearly 1200000 tons of mixed fertilizer has been produced yearly by the following process:—calcium superphosphate, ammonium sulfate and potassium chloride are mixed, ammoniated so as to neutralize the free phosphoric acid in superphosfate, granulated between 3 and 20 meshes with sprayed water, dried in a rotary drier so as to have 2～3% free water, cooled to 40～60°C by rotary cooler, kept in storage pile for days or weeks and then packed. Ikeno[1] reported that ammonium syngenite and monoammonium phosphate were formed in 8-8-7 mixed fertilizer. No other report is found concerning the fertilizer.

In the present work the mineral content of the products having various $N:P_2O_5:K_2O$ ratios and reactions during the production process were investigated so as to clarify the cause of caking of products which often takes place in the storage pile, the action of water in the products which must be known for calculation of material balance, and other problems concerning the fertilizer have been studied.

Experimental and Results

Mineral Content of Products.—It was clarified by X-ray diffraction that commercial mixed fertilizers (Table I) were mainly composed of potassium ammonium syngenite (crystalline solution of potassium syngenite $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ and ammonium syngenite $[(NH_4)_2SO_4 \cdot CaSO_4 \cdot H_2O]$, monoammoniumpotassium phosphate (crystalline solution of monoammonium phosphate $NH_4H_2PO_4$ and monopotassium phosphate KH_2PO_4), ammonium chloride and calcium sulfate anhydride. The minerals used as raw materials such as monocalcium phosphate monohydrate, ammonium sulfate and potassium chloride were not at all or were only slightly detected in the products. The amount of these minerals in the products was determined by X-ray diffractometer using spinel $MgO \cdot Al_2O_3$ as inner standard.

Synthesis of Standard Samples. — a) *Inner Standard.*—By preliminary tests it was found that spinel $MgO \cdot Al_2O_3$ was suitable as inner standard. A mixture of equal mole of refined magnesia and alumina was heated for 30 min. at 1600～1670°C. Spinel was formed almost completely. The product contained very few other minerals.

b) *Calcium Sulfate Anhydride.*—Calcium carbonate was treated with concentrated sulfuric acid.

c) *Syngenite.*—Ammonium sulfate or potassium sulfate or various mixtures of both of these was mixed with a theoretical amount of calcium sulfate anhydride and excess of water, heated at 45°C on a water bath and dried. Addition of water and drying were repeated until the single salts disappeared and syngenite or a homogeneous crystalline solution of syngenite was formed.

d) *Monoammoniumpotassium Phosphate.* — Monoammonium phosphate and monopotassium phosphate were mixed at various ratios, the mixture being wet with water, heated at 45°C on water bath

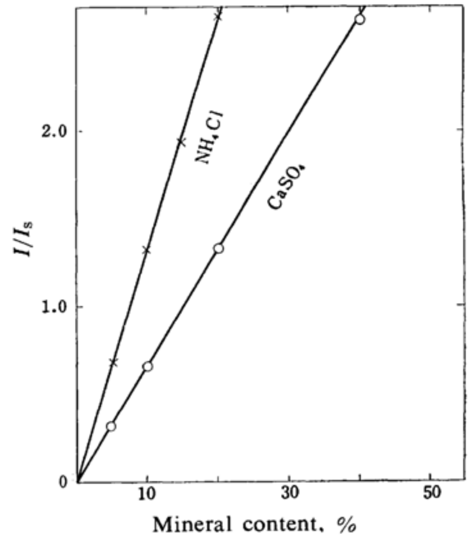

Fig. 1. Calibration curves of ammonium chloride and calcium sulfate anhydride.

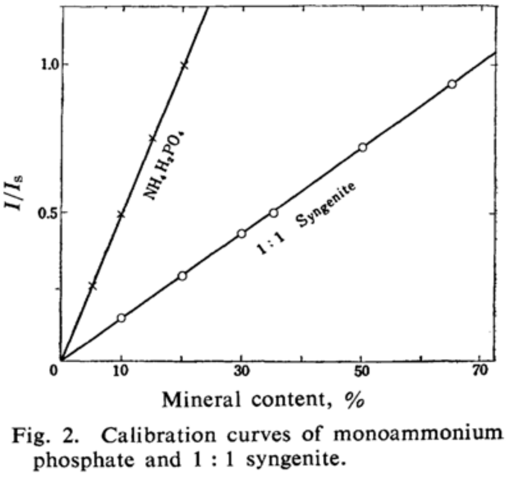

Fig. 2. Calibration curves of monoammonium phosphate and 1 : 1 syngenite.

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[1] R. Ikeno and Y. Shimomura, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 63, 78 (1960).

and dried. A homogeneous crystalline solution was formed easily.

Method of Determination.—The Amount of each salt was determined measuring the diffraction peaks of the following angle (2θ by Cu ray): spinel 36.8°, crystalline solution of syngenite around 9°, monoammoniumpotassium phosphate around 16.6°, ammonium chloride 32.6°, calcium sulfate anhydride 25.4°, ammonium sulfate 20.4° and potassium chloride 28.3°. One handred parts of a mixture of 1 : 1 syngenite (crystalline solution of ammonium and potassium syngenite 1 : 1 by weight), monoammonium phosphate, ammonium chloride and calcium sulfate anhydride were mixed with 25 parts

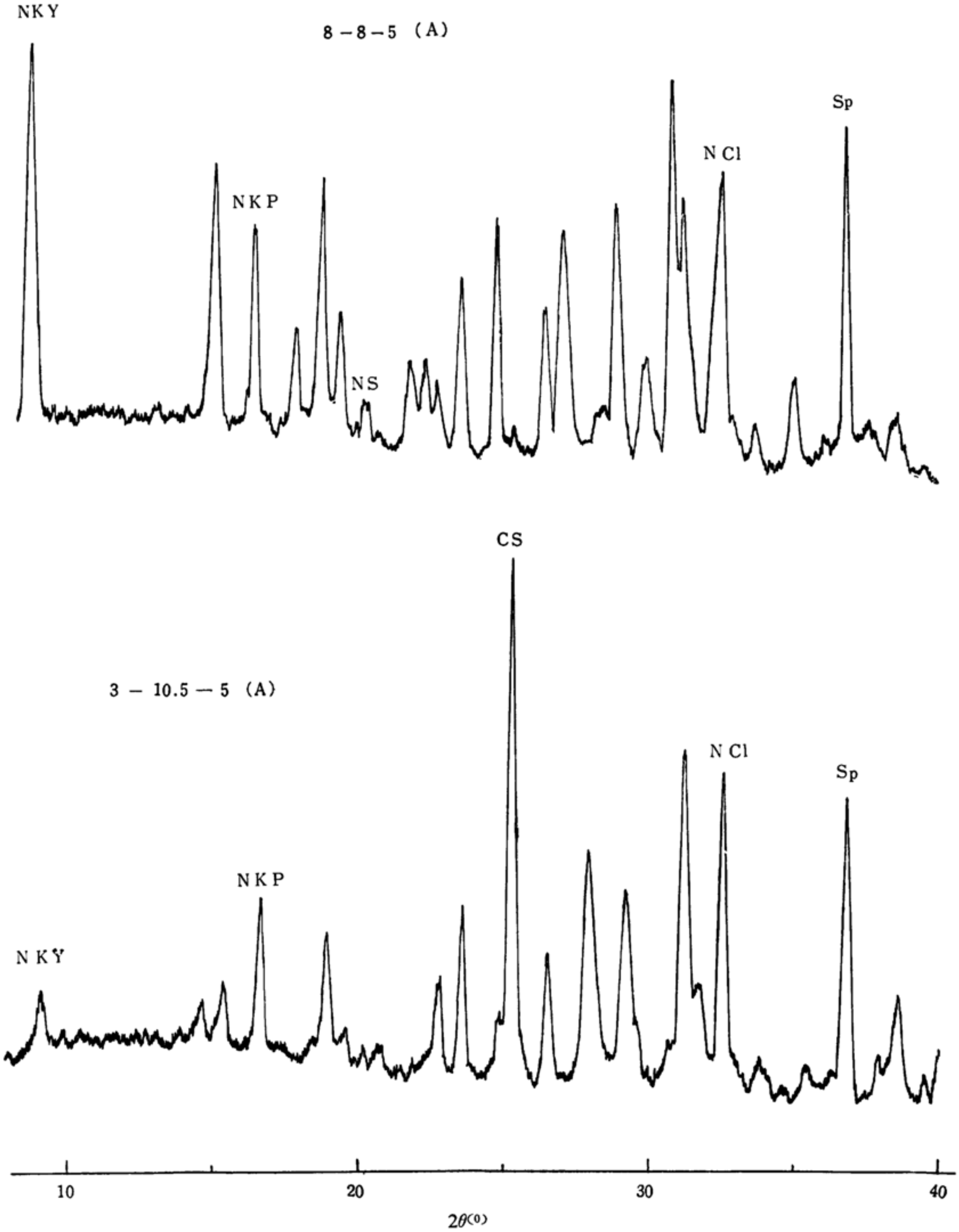

Fig. 3. X-ray diffraction patterns of mixtures of commercial fertilizers, 100 parts, and spinel, 25 parts (Cu ray, Ni filter).

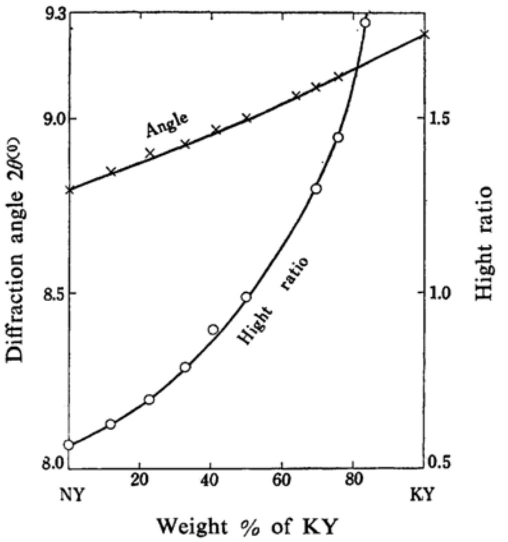

Fig. 4. Relation between weight ratio of ammonium syngenite (NY) component and potassium syngenite (KY) component in their crystalline solution and diffraction angle of center of the peak and also the ratio of height of the peak of 1 : 1 syngenite and that of other syngenite.

of spinel and were recorded by X-ray diffractometer. Calibration curves thus obtained are illustrated in Figs. 1 and 2.

One handred parts of mixed fertilizer and 25 parts of spinel were mixed and recorded by X-ray diffractometer (Fig. 3). The content of ammonium chloride and of calcium sulfate anhydride were determined by Fig. 1.

Figure 4 or 6 was plotted by measurement of various crystalline solution of syngenite or phosphate. The NH_4/K ratio and amount of syngenite or phosphate in commercial fertilizer were determined using the relations of Figs. 2 and 4 or 6.

Results of determination of commercial fertilizer are shown in Table I. These samples contained 1~3% free water measured by weight loss on heating for 3 hr. at 100°C (Table II). A small part of salt was dissolved in the water and was not determined by X-ray. A sample 3-10-10 (C) contained a considerable amount of potassium chloride which was not detected in other samples. The samples contained less than 3% ammonium sulfate. No monocalcium phosphate monohydrate was detected in any sample. Considering these facts together with the results of Table II it is known that the quantitative analysis by X-ray was performed fairly accurately.

Reactions during Production Process.—Mixed fertilizer 8-8-6 was prepared in the laboratory under conditions similar to that of a large scale plant.

TABLE I. MINERAL CONTENT (%) OF COMMERCIAL MIXED FERTILIZER PRODUCED IN THREE PLANTS (A, B and C)

Sample	$CaSO_4$	NH_4Cl	NKP			NKY			Total
			Sum	NP	KP	Sum	NY	KY	
8-8-5 (A)	1.7	6.5	12.5	11.9	0.6	58.8	41.2	17.6	81.0
6-9.5-5 (A)	12.3	6.7	14.8	14.1	0.7	44.8	28.0	16.8	78.6
3-10.5-5 (A)	27.5	8.5	15.6	11.2	4.4	24.6	5.7	18.9	76.2
8-8-5 (B)	6.7	6.5	14.1	14.1	0	51.8	36.2	15.6	80.7
8-8-6 (C)	3.4	7.2	14.7	14.3	0.4	66.4	41.5	24.9	91.7
8-7-8 (C)	3.3	10.5	12.2	12.0	0.2	65.8	33.2	32.6	91.8
6-9-6 (C)	20.1	7.5	14.8	13.8	1.0	47.7	25.3	22.4	90.1
8-7-8 (C)	3.4	11.5	13.1	12.9	0.2	57.3	30.4	26.9	85.3
3-10-10 (C)	31.6	5.7	21.6	15.0	6.6	25.3	4.8	20.5	84.2

NP=monoammonium phosphate, KP=monopotassium phosphate,
NKP=crystalline solution of NP and KP, NY=ammonium syngenite, KY=potassium syngenite,
NKY=crystalline solution of NY and KY

TABLE II. COMPARISON OF N, P_2O_5 AND K_2O CONTENT DETERMINED BY CHEMICAL ANALYSIS (G) AND BY X-RAY ANALYSIS (X) OF TABLE I

Sample	N		P_2O_5		K_2O		Free water
	X	G	X	G	X	G	
8-8-5 (A)	6.88	8.76	7.65	8.79	5.55	5.56	3.0
6-9.5-5 (A)	5.92	6.96	9.07	10.34	5.35	5.53	3.1
3-10.5-5 (A)	4.07	4.05	9.21	10.61	7.26	7.68	5.5
8-8-5 (B)	6.46	8.50	8.70	9.10	4.74	5.31	1.4
8-8-6 (C)	7.11	8.33	9.04	9.10	7.70	6.25	0.8
8-7-8 (C)	7.00	8.01	7.54	7.53	9.98	10.01	1.9
6-9-6 (C)	5.78	6.02	9.03	9.10	7.16	7.20	2.2
8-7-8 (C)	7.13	8.70	8.10	8.12	8.25	8.60	0.9
3-10-10 (C)	3.72	3.80	12.70	11.46	6.47	10.70	2.5

The mineral content of samples during the course of preparation was determined by X-ray. Samples of each process in a large scale plant were investigated, too.

Superphosphate (−20 mesh, P_2O_5 17.56%, free water 12.02%) 356 g., potassium chloride (red colored, −42 mesh) 73.5 g. and ammonium sulfate (−42 mesh) 266 g. were mixed and put in a porcelain rotary drum (26×26 cm.). After 74 cc. of 4.75% aqueous ammonia and 15 cc. of water were sprayed the mixture was granulated between 4 and 10 mesh and dried in an air oven at 130°C for 15, 30, 45 and 60 min. Fifty grams of the sample dried for 60 min. (containing 2.91% free water) was put in a 50 cc. stoppered bottle and kept at 50°C for 5 days and then at room temperature for 10 days. The mineral content of samples just after mixing, granulation, drying and keeping for each time were determined by X-ray. The free water of samples was measured by weight loss on drying powdered samples for 3 hr. at 100°C.

It was known by preliminary tests that when the sample containing much water was powdered finely and recorded by X-ray a remarkable change took place in the sample during this procedure. In order to determine the mineral content of samples without the change during analytical procedure the samples were washed with pure ethyl alcohol, filtered, dried at room temperature in vacuum desiccator in several minutes and tested by X-ray diffractometer. In this case the free water of samples was eliminated and the salts dissolved in the water were crystallized. The mineral content of the original sample was calculated multiplying the value of X-ray analysis by (100-free water %)/100. The results are shown in Fig. 7.

Figure 7 illustrates that the following chemical reactions take place partly soon after the mixing of raw materials and extensively by the addition of ammonia and water.

$$Ca(H_2PO_4)_2 \cdot H_2O+(NH_4)_2SO_4 = 2NH_4H_2PO_4+CaSO_4+H_2O \qquad (1)$$

$$(NH_4)_2SO_4+CaSO_4+H_2O + (NH_4)_2SO_4 \cdot CaSO_4 \cdot H_2O \qquad (2)$$

$$CaSO_4 \cdot 1/2H_2O+(NH_4)_2SO_4+1/2H_2O = (NH_4)_2SO_4 \cdot CaSO_4 \cdot H_2O \qquad (3)$$

$$H_3PO_4+NH_4OH=NH_4H_2PO_4+H_2O \qquad (4)$$

$$2KCl+(NH_4)_2SO_4=K_2SO_4+2NH_4Cl \qquad (5)$$

$$K_2SO_4+Ca(H_2PO_4)_2 \cdot H_2O = 2KH_2PO_4+CaSO_4+H_2O \qquad (6)$$

$$K_2SO_4+CaSO_4+H_2O=K_2SO_4 \cdot CaSO_4 \cdot H_2O \qquad (7)$$

$$mKH_2PO_4+nNH_4H_2PO_4 \rightarrow \text{crystalline solution} \qquad (8)$$

$$r[(NH_4)_2SO_4 \cdot CaSO_4 \cdot H_2O] + s(K_2SO_4 \cdot CaSO_4 \cdot H_2O) \rightarrow \text{crystalline solution} \qquad (9)$$

$$2KH_2PO_4+(NH_4)_2SO_4 \cdot CaSO_4 \cdot H_2O = 2NH_4H_2PO_4+K_2SO_4 \cdot CaSO_4 \cdot H_2O \qquad (10)$$

Potassium sulfate formed by reaction 5 reacts

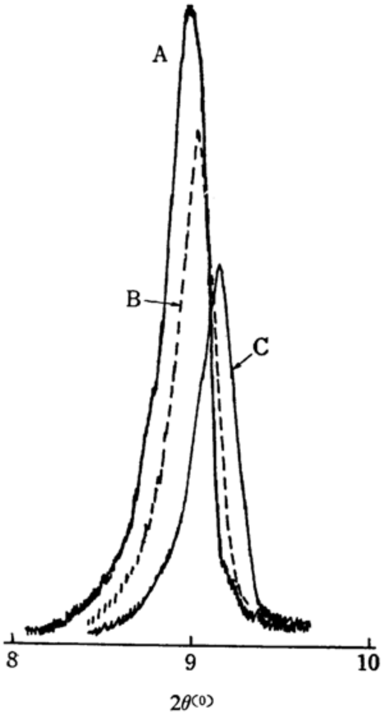

Fig. 5. Change of diffraction peak of crystalline solution of syngenite.
Weight ratios of ammonium and potassium syngenite are: A 66:34; B 50:50; C 24:76.

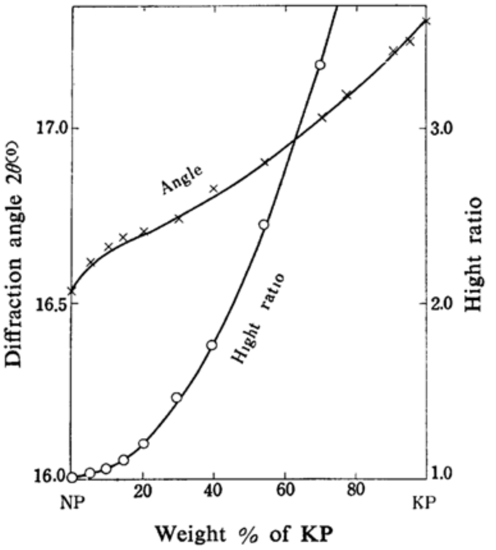

Fig. 6. Relation between weight ratio of monoammonium phosphate (NP) component and monopotassium phosphate (KP) component in their crystalline solution and diffraction angle of center of the peak and also the ratio of height of the peak of NP and that of the crystalline solution.

immediately to form potassium syngenite (7) and monopotassium phosphate(6) and does not actually exist in samples. Reactions 1-9 were almost completed when the granules were dried for 15 min. in a 130°C oven. At this time the free water of the sample was 8.52%.

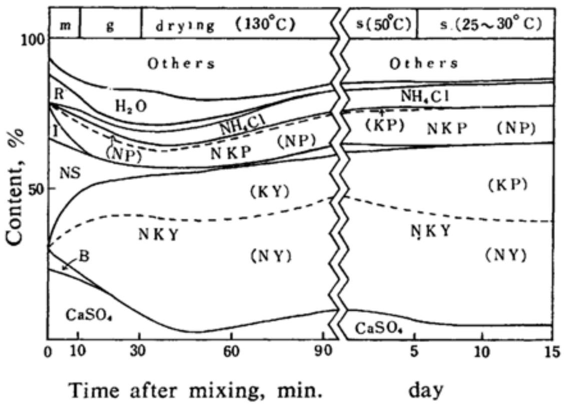

Fig. 7. Change of mineral content of samples in the midst of production process.
m = mixing, g = granulation, s = storing in sealed bottles, R = KCl, I = $Ca(H_2PO_4)_2 \cdot H_2O$, NP = $NH_4H_2PO_4$, KP = KH_2PO_4, NKP = crystalline solution of NP and KP, NS = $(NH_4)_2SO_4$, KY = $K_2SO_4 \cdot CaSO_4 \cdot H_2O$, NY = $(NH_4)_2SO_4 \cdot CaSO_4 \cdot H_2O$, NKY = crystalline solution of NY and KY, B = $CaSO_4 \cdot 1/2H_2O$.

It was clarified that by further drying a part of syngenite was decomposed to form calcium sulfate anhydride and ammonium sulfate. When dried for 60 min. the free water of the sample was 2.91% and the content of ammonium sulfate and calcium sulfate anhydride increased to a fair extent (Fig. 7). After being stored for days in a sealed bottle at 50°C the free water and those minerals decreased to form syngenite and the grains of the sample slightly adhered to each other forming a cake. When the granulated sample was dried at 120°C for 60 min. the free water content of the sample was 4.32%. Decomposition of syngenite took place similarly. After being stored for days at 50°C the grains adhered to each other more firmly than they did in the above sample.

The reaction 10 took place gradually and continued even in storing at room temperature. By this reaction NH_4/K ratio of crystalline solution of syngenite decreased and that of monophosphate increased.

Samples of 8-8-5 mixed fertilizer in the midst of each process of large scale production were tested in the same way. It was clarified that the above reactions took place similarly but often more slowly than in the laboratory test, perhaps because the raw materials were not mixed so well as in the laboratory. A greater amount of calcium sulfate anhydride and ammonium sulfate and less syngenite were contained in the sample before piling. The sample after being piled and caked contained a very small amount of free water and these salts.

Thermal Decomposition of Syngenite.—Figure 8 illustrates the weight loss of synthetic ammonium and potassium syngenite and crystalline solution of equal weight of the two when heated at a rate of 3～4°C/min. Ammonium syngenite was decomposed over 110°C. Over 160°C ammonium sulfate was volatilized. 1 : 1 syngenite or potassium syngenite was decomposed over 120°C or 240°C respectively. The syngenite contained in commercial fertilizer 8-8-6 or 8-8-5 resembled 1 : 1 syngenite and was not decomposed by heating for hours at 120°C. Ammonium syngenite was not decomposed by heating for hours at 100°C. However, it was clarified that the syngenite just after its formation in mixed fertilizer e. g. just after the granulation or at the begining of drying was partly decomposed even by heating at 100°C, perhaps because syngenite crystals had not grown well and a small amount of impurities such as HPO_4^{2-} instead of SO_4^{2-} was contained in the crystal.

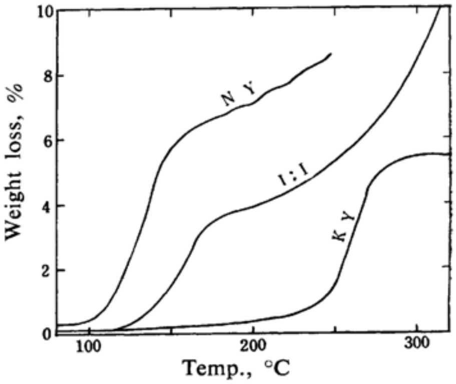

Fig. 8. Thermal decomposition of syngenite. NY = ammonium syngenite, KY = potassium syngenite, 1 : 1 = crystalline solution of the two 1 : 1 by weight.

To determine exactly the free water content of such samples by heating at 100°C, the amount of crystallization water lost by the heating must also be measured determining the amount of syngenite decomposed.

Discussion

It seems that syngenite, especially ammonium-rich syngenite plays an important role concerning the caking of products in a storage pile. In the preparation of standard samples it was observed that potassium rich syngenite was formed quickly and had little tendency of hardening and that ammonium-rich syngenite was formed slowly and hardened. Moreover, ammonium-rich syngenite is apt to decompose on drying and recrystallize during piling.

It has been known that mixed fertilizers such as 8-7-8, 8-8-6 and 8-8-5 are apt to form a hard cake and that the fertilizers such as 3-10-10, 3-10.5-5 etc. have little tendency of caking in a storage pile. This is attributable to the fact that the latter contain less and the former much ammonium syngenite component.

In large scale plants the granules are often dried in shorter time at a higher temperature than was done in the laboratory experiment. Thermal decomposition of syngenite must take place remarkably on the surface of grains which are dried enough and reach a high temperature. Free water remains in the inner part of the grains and gradually disperses to the surface to cause the recrystallization of syngenite and the caking of products. By the crystallization of syngenite the free water content of the products is reduced and a part of the salts dissolved in the water is crystallized promoting the formation of a hard cake.

The reaction 10 takes place successively in a storage pile. When the raw materials were not powdered finely or mixed well, reactions 1-9 are not completed before piling but occur continuously in the storage pile. All of these reactions are promoted by free water in the granules.

In order to prevent the caking of products (1) free water of the granules must be reduced as far as possible by drying, (2) drying at high temperature must be avoided so as to depress the thermal decomposition of syngenite, (3) the raw materials had better be powdered and mixed well so that the reactions 1-9 are almost finished before piling, and (4) the dried sample had better be cooled to a lower temperature. Of course it is desirable not to pile the products too high.

It was observed that ammonium chloride was volatilized slightly by heating at 130°C. In the drier of the large scale plant a small amount of ammonium chloride must be volatilized. Also for this reason the granules must not be dried at a high temperature.

Measurement of the amount of free and crystallization water of the products is nesessary for calculation of material balance. It was clarified that water of crystallization was contained only in syngenite and that its amount could be measured by X-ray determination of syngenite. The free water content of products stored for more than a week after granulation could be measured almost exactly by drying the samples for 3 hr. at 100°C. To measure the free water content of samples soon after production by the above method the loss of crystallization water by the drying must also be measured, determining the amount of syngenite before and after the drying. By such a method the material balance of mixed fertilizer could be calculated exactly.

Summary

The mineral content of mixed fertilizer produced with calcium superphosphate, ammonium sulfate and potassium chloride and also the reactions during the production process were investigated by X-ray diffraction.

It was observed that remarkable reactions took place between monocalcium phosphate, calcium sulfate, ammonium sulfate and potassium chloride by the addition of water for granulation. At the beginning of drying of the wet granules these minerals almost disappeared to form ammonium chloride and crystalline solutions of ammonium and potassium syngenite and those of monoammonium and monopotassium phosphate.

The syngenite thus formed decomposed partly by further drying and again formed while the product was placed in a storage pile. It seems that the caking of the product which often occurs in a storage pile is caused mainly by the crystallization of syngenite which decreases the amount of free water in the product and makes other salts crystallize at the same time.

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Department of Industrial Chemistry
Faculty of Engineering
Chuo University
Bunkyo-ku, Tokyo